

Proofs of the Presence of γ -Glutamyl-S-(1-propenyl)-sulphoxide and Cycloalliin as Original Compounds in Onion (*Allium cepa*)

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In a recent communication¹ it was reported that the γ -glutamyl peptide 4 isolated from onion was probably γ -L-glutamyl-S-(1-propenyl)-cysteine sulphoxide. This conclusion has now been confirmed. After enzymic hydrolysis of the peptide, a larger amount of the sulphur-containing amino acid was obtained in crystalline form (long needles), and its identity with the (+)-S-(1-propenyl)-cysteine sulphoxide isolated as a free amino acid by Virtanen and Spåre² could be conclusively proved. The IR-spectra were identical and the $[\alpha]_D^{25}$ was $+74.5^\circ$ (in water). On the basis of the optical rotation, it can be concluded that this cysteine derivative is also present in the peptide as a sulphoxide, since the formation of the sulphoxide from thioether during the treatment would lead to a preparation with a racemic sulphur atom. This is the first γ -glutamyl peptide isolated by us in which the cysteine derivative is in the form of a sulphoxide.

Because cycloalliin was recently found by Virtanen and Spåre² to be formed easily from the lachrymatory precursor, S-(1-propenyl)-cysteine sulphoxide, at a slightly alkaline reaction, the possibility existed that cycloalliin was formed during the elution of the amino acids with ammonia from the Amberlite IR-120 column, and was not present as such in the onion. To prove this, an onion was cut in two and one half immediately placed in 6 N HCl. After 24 hours' heating in a sealed tube at 105°C , when both the free and the bound lachrymatory precursor is destroyed and cycloalliin is partly reduced to the corresponding thioether, partly oxidized to 2-methyltaurine and cysteic acid, the amino acids were separated on an Amberlite IR-120 column. On a two-dimensional paper chromatogram (butanol-acetic acid-water and phenol-water (NH_3)) the spot of the thioether of cycloalliin was found. On the basis of this result, the onion contains cycloalliin as an original compound although additional cycloalliin is formed from the lachrymatory precursor during the isolation.

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References

1. Virtanen, A. I. and Matikkala, E. J. *Suomen Kemistilehti B* **34** (1961) 84.
2. Virtanen A. I. and Spåre, C.-G. *Ibid.* **34** (1961) 72.